

COMPARATIVE CORROSION STUDIES ON ALUMINA PLUS CALCIA STABILIZED ZIRCONIA COATINGS APPLIED TO AL6061 AND CAST IRON SUBSTRATES

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ABSTRACT

In the present investigation, a comparative study on Alumina plus calcia stabilized Zirconia coatings applied on Al-6061, and cast iron substrates have been done and called coating system. The top coat thicknesses were varied in 100, 200, and 300µm for both the coating systems. The coating was achieved using Plasma Spray Technique (PST). The test was conducted as per ASTM B117 standard using Salt Fog Spray Technique. The samples were exposed to saline, aqueous NaCl solution at PH 6.7 for the duration of 24 hrs. Results obtained from SEM and EDX analysis found that as the coating thickness increases, the porosity of the top coat decreases and it also inhibits the corrosion phenomenon. The top coat of 100µm in the case of cast iron subjected to accelerated corrosion due to higher porosity and less thickness. The mechanism of corrosion has also been discussed in detail which may be helpful for the material scientist and researchers.

KEYWORDS: Salt Fog Spray, Alumina Plus Calcia Stabilized Zirconia & Corrosion

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1. INTRODUCTION

Composite coatings are primarily used to shield the functional components that have to work under hostile environment. Composite coating finds applications in the numerous engineering areas viz. automobiles, aerospace, chemical, textile, and oil & gas industries etc., owing to good tribology chemical properties. Previous studies have shown that coatings severely exaggerated by the methods and coating variables viz. rate of deposition, coating speed, coating distance, the concentration of the particles, etc. These variables often leads to frequent imperfections like agglomeration of the semi and completed melted splats making the surface rough also localized activation of the coating surface (stress risers), porosity, non-uniformity in coatings etc. Other features such as coating compositions, thickness of the coatings and pre and post treatment methods of the coating significantly affect the corrosion resistance [1]. Due to aforesaid problems the composite coatings limit its uses in material science and technology. It has been noticed that the degree of weight loss and rate of corrosion severely affected by the reaction time, temperature, concentration medium, heat transfer, mass transfer, etc. Studies shown that pure ceramics or composite ceramic if appropriately developed it may exhibit high resistant to corrosion along with extraordinary mechanical and thermal stability when operated at elevated temperature. The performance and applications of composite powders are yet not explored thoroughly. Many research activities has happened the field of ceramic to

control its reactivity in acidic/basic medium. A corrosion study has been done using NaCl solution at 1200 K for 24 hours on oxide-based ceramics viz. Al_2O_3 , SiO_2 , ZrO_2 , and found no weight loss [2]. A Salt fog corrosion study has been done on yttria-stabilized zirconia 8% Y_2O_3 + 92% Zr_2O_3 , and Ceria stabilized Zirconia (8% Y_2O_3 + 67% Zr_2O_3 + 25% CeO_2) and found that Ceria Stabilized Zirconia has better corrosion resistance [3]. Similar kind of corrosion test was performed using NaCl at 1000 °C on Al_2O_3 and Cr_2O_3 and found little mark of oxidation on that Al_2O_3 compared to Cr_2O_3 [4]. In another study, the corrosion behavior of ceramic coated steel was judged for different coating thickness and found that the corrosion of the coatings primarily depends on coating temperature [5]. Hot corrosion study on 8mol% Yttria Stabilized Zirconia (8YSZ) for 40 hours at 1050 °C were carried out in presence of V_2O_5 and Na_2SO_4 salt solution and found delamination of the 8YSZ coat happened due to the stress developed in yttria (Y_2O_3) in the admixture of 8YSZ [6]. In one of the study it has been found that Air Plasma Spray coatings provide strong passivation towards oxidation, but due to microporosity, the corrosion resistance ability reduced [7]. The chemical stability of ZnO applied on steel reinforced in concrete investigated using 3.5% NaCl and found that ZnO noticeably improve the corrosion resistance[8] Similar type of electrochemical experiment carried out on pure Titanium and Ti_3SiC_2 in 3.5% NaCl aqueous solution and found Ti_3SiC_2 as excellent corrosion inhibitor[9]. An interesting investigation of Ni-P-SiC coatings reveals that the nanoparticles distribution may influence the corrosion phenomenon[10]. A metallic cylinder liners which is one of the a critical component of internal combustion engine have to work under elevated temperature and frequently experience abrasive wear, corrosion/oxidation this leads to economic burden to the manufacturing industries. In view of this, an attempt has been made to develop and improve a composite material which shows passivity when operated under sensitive conditions.

To achieve best coating thickness for final passivation, the coating thicknesses were varied in 100, 200 & 300 μm . Salt fog spray corrosion study technique was used to envisage the suitability of the coating. In this experimental study, an endeavour has been made to explain the mechanism of corrosion of the special composite coatings (Al_2O_3 + ZrO_2 .5CaO) blended in 50:50 proportion using ball mill technique and applied on Al6061 and Gray cast Iron substrates using Atmospheric Plasma spray coating technique. The motive for selecting pure ceramic is that oxide-based ceramic offer high resistance to diffusion to any chemical reactivity.

2. EXPERIMENTAL DETAILS

2.1 Coating Methodology and Sample Preparation

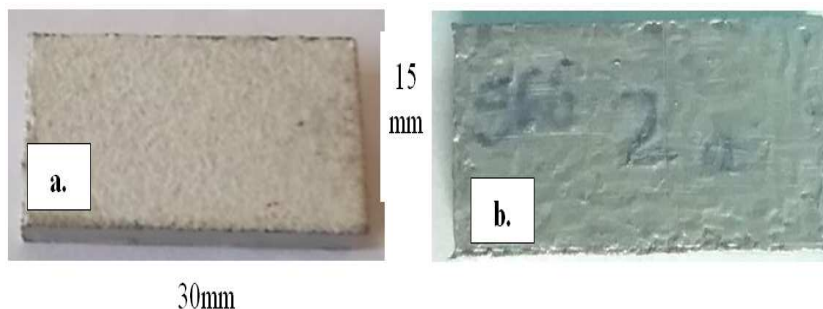
Air Plasma sprays (APS) coating technique was used for the coating applications. The APS machine specifications and spray parameters adopted for different coating materials are shown in Table 1 and 2 respectively. A rectangular specimen of sizes 30 mm \times 15 mm was developed for the corrosion test purpose refer to Figure 1. Total six samples, three for each Al-6061 and Gray Cast Iron were developed. The top coat thicknesses were only varied in 100, 200, & 300 μm for both the coating systems. The schematic of a coating system for Al-6061 and GCI shown in Figure.2 and 3 respectively.

Table 1: Air Plasma Spray Machine Specifications

Specifications	Parameters
Plasma gun	3 Nylon Brush
Nozzle temperature	10,000 °C
Current	500 amps
Voltage	65-70 volts
Powder feed	45-50 gms/mint
Spray distance	50 -78 mm

Table 2: Air Plasma Spray Parameters

Materials	Primary gas (Argon) Pressure(Bar)	Secondary gas (Hydrogen) Pressure (Bar)	Carrier gas Argon flow (lpm)	Current (amps)	Voltage (volts)	Spray distance (mm)
Al ₂ O ₃ + ZrO ₂ .5CaO	3.7	3.45	35	500	65	65-76
Fe38Ni10Al	6.9	3.30	35	500	65	50-76
Al25Fe7Cr5Ni	6.9	3.30	35	500	65	50-76
Al ₂ O ₃ 30(Ni20Al)	3.7	3.45	35	500	65	65-76



**Figure 1(a): Al₂O₃. ZrO₂5CaO Coated Top Coat
(b) Protective Paint Coatings**

Top Coat (100 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)	Top Coat (200 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)	Top Coat (300 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)
Bond Coat 2(50 μm) (Cermet) Al ₂ O ₃ 30(Ni20Al)	Bond Coat 2 (50 μm) (Cermet) Al ₂ O ₃ 30(Ni20Al)	Bond Coat 2(50 μm) (Cermet) Al ₂ O ₃ 30(Ni20Al)
Bond Coat 1 (50 μm) Metallic Powder Al25Fe7Cr5Ni	Bond Coat 1(50 μm) Metallic Powder Al25Fe7Cr5Ni	Bond Coat 1(50 μm) Metallic Powder Al25Fe7Cr5Ni
Substrate (Al6061)	Substrate (Al6061)	Substrate (Al6061)

Figure 2: Coating System for Al-6061

Top Coat (100 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)	Top Coat (200 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)	Top Coat (300 μm) Pure Ceramic (ZrO ₂ .5CaO+Al ₂ O ₃)
Bond Coat (50 μm) (Metallic Powder) Fe38Ni10Al	Bond Coat(50 μm) (Metallic Powder) Fe38Ni10Al	Bond Coat(50 μm) (Metallic Powder) Fe38Ni10Al
Substrate (Gray Cast Iron)	Substrate (Gray Cast Iron)	Substrate (Gray Cast Iron)

Figure 3: Coating System for Gray Cast Iron

2. 2 Coating Characterization

The coating characterization is done on Zeiss Evo 18 special edition machine shown in Figure. 4. The SEM and EDS machine specifications are shown in Table 3.

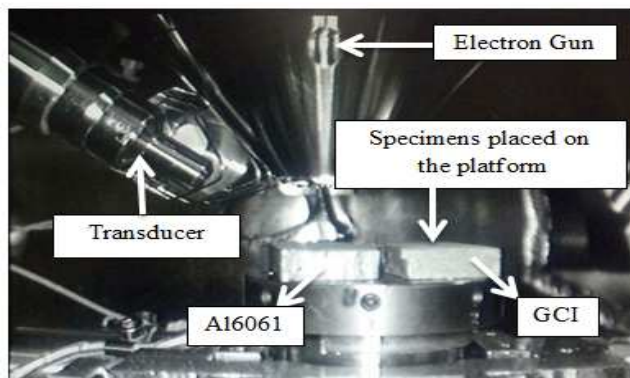


Figure 4: Scanning Electron Microscope

Table 3: SEM / EDS Machine Specifications

Parameters for Zeiss Evo 18 special edition	
Filament	Tungsten
Secondary e-image resolution	50 NM
Tilt	0 - 60 Degree
Rotation	360 Degree
EHT	200V - 30KV
Magnification	Up to 50K ~ 100K (Depends on sample)

2. 3 Corrosion Test Procedure

ASTM B117 [11] Salt fog spray corrosion (SFSC) test procedure was adopted to do the corrosion investigation. The test setup is shown in Figure 5. The coated specimens were kept in a chamber exposed continuously to 5% NaCl aqueous salt solution to a period of 24 hours. The test was conducted at 35 ± 1 °C, and a pH of 6.7 was maintained throughout the experiment. The initial weight of the specimens was taken using electronic measuring device (accuracy lies in the range of ± 0.005 gm) also images of the top coat captured using the high-resolution camera. After every 8 hours, weight loss and corresponding top coat images were taken. Corroded specimens were only investigated using SEM and EDX analysis to confirm the corrosion phenomenon and mechanism of corrosion discussed in result and discussion section.



Figure 5: Salt Fog Sprays Corrosion Setup

3. RESULTS AND DISCUSSIONS

The Visual inspection followed by weight measurement of the test specimens clearly shows that the top coat of 100µm of both the coating system subjected to only corrosion. Relatively more corrosion product acknowledge in case of GCI coating system refer Figure. 6 a & d. The reason for corrosion attributed to less coating thickness and high porosity. In case of GCI, the top coat and bond coat porosity found to be 1.90% and 2.75% respectively against 1.58% and 0.83% in case of the Al-6061 substrate. The reason for the differences in porosity attributed to change in parameters such as substrate temperature, spraying speed, spray distance and particle size can influence the rate of corrosion. Figure. 7 & 8 exhibits an average porosity on the top and bottom coat. No weight loss acknowledge in any of the coating systems. The corrosion mechanism can be understood as follows: Due to less coating thickness and relatively high porosity, the aqueous solution of sodium chloride easily diffused in the region of bond coat thereby reacting with the water due to which NaCl dissociates into ionic form Na^+ and Cl^- due to which electron mobility increases and also conductivity increases. The free electrons interact with the iron content in the bond coat Fe38Ni10Al, transforming Fe to Fe^{2+} or Fe^{3+} . The ionic form of iron interact with the available oxygenating element, in this case, oxygen and moisture(water vapor) thus corrosion appeared as hydrated Iron Oxide ($2\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) refer Figure.9 & 10. In the present case, the availability of oxygenating elements is more in case of GCI coating system i. e. compare to Al-6061 refer Fig. 11 a & b. Thickness above 100µm is found less susceptible to corrosion. The corrosion mechanism can be understood with the equation 1,2,&3.



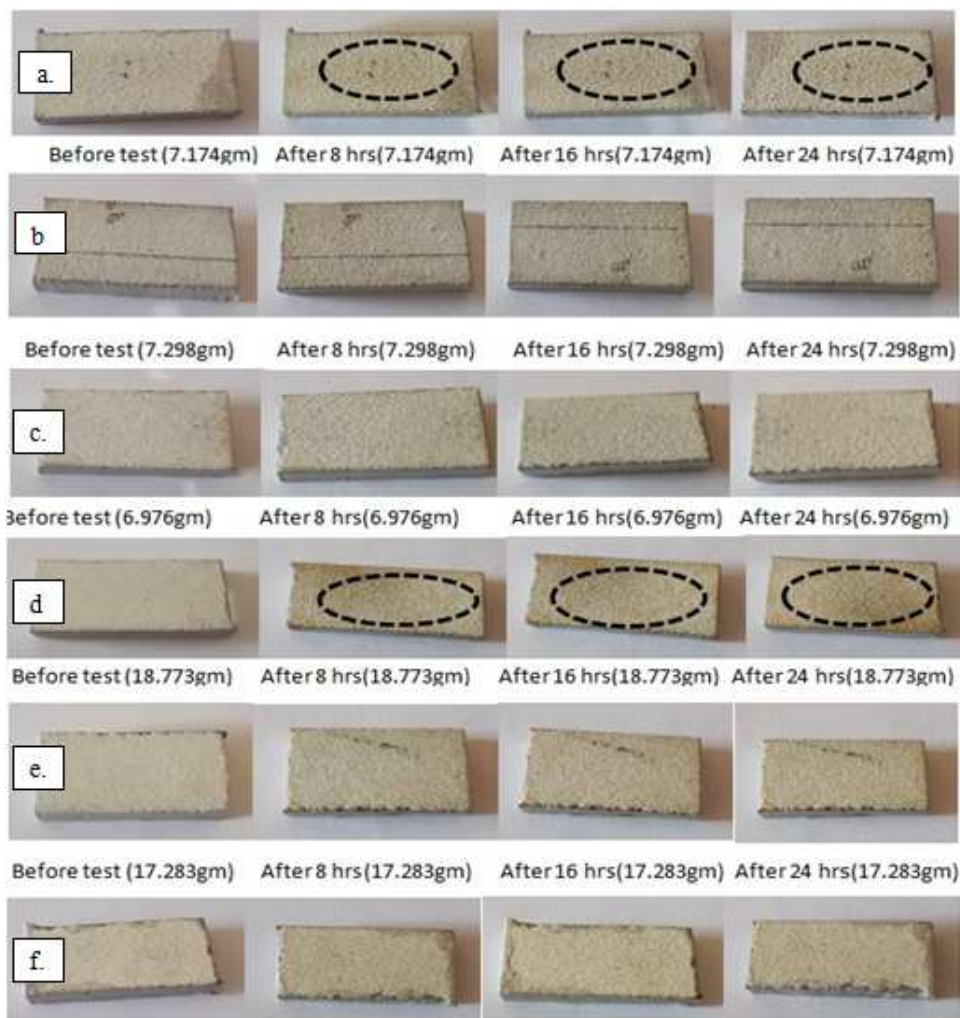


Figure 6: Illustration of the Surface Corrosion and Corresponding Weights Loss for Al-6061: (a) 100μm (b) 200μm (c) 300μm & GCI : (d) 100μm (e) 200μm (f) 300μm

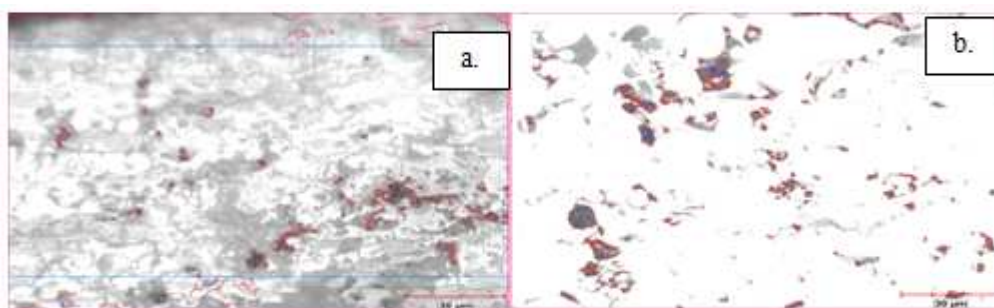
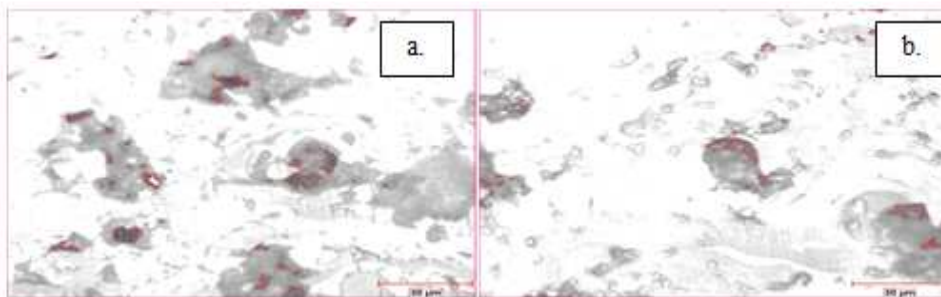
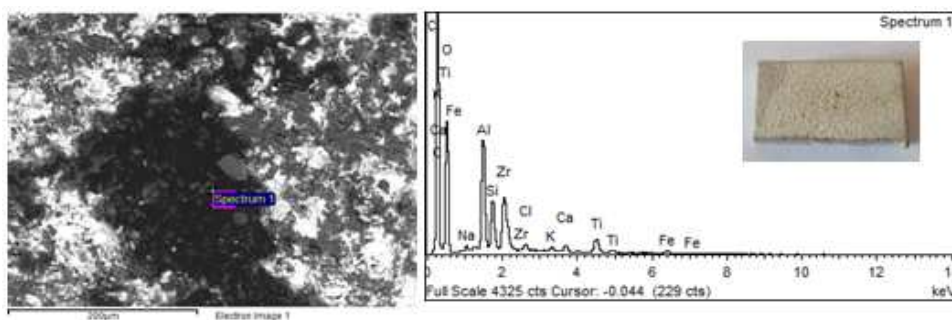


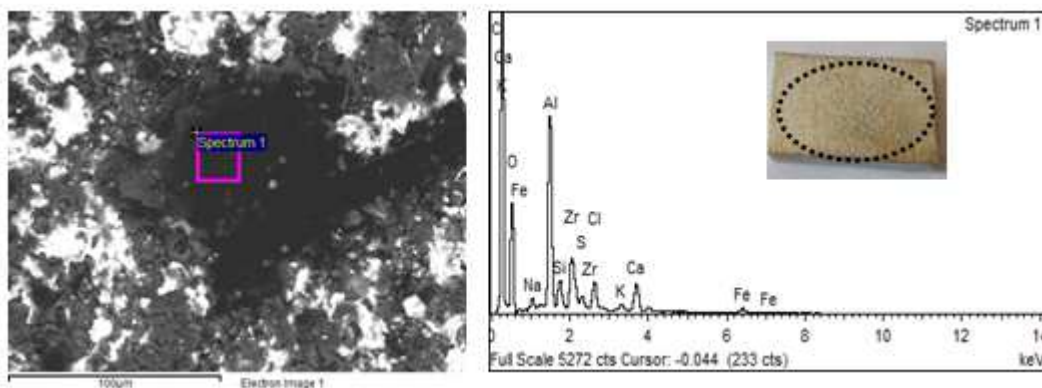
Figure 7: Average Micro Porosity of GCI Coating System (a) 1.90 % Top Coat (b) 2.75% Bond Coat of the Specimen



**Figure 8: Average Micro Porosity of Al-6061 Coating System
(a) 1.58 % Top Coat (b) 0.83% Bond Coat**



**Figure 9: SEM Morphology and Elemental Abundance over the Localized Corroded
Region Acknowledged on the Al-6061 Coating System**



**Figure 10: SEM Morphology and Elemental Abundance over the Localized Corroded
Region Acknowledged on the GCI Coating System**

Element	Weight%	Atomic%	Element	Weight%	Atomic%
CK	53.11	64.15	OK	50.85	70.97
OK	34.96	31.70	NaK	1.52	1.48
NaK	0.22	0.14	AlK	17.23	14.26
AlK	3.22	1.78	SiK	2.77	2.20
SiK	1.52	0.78	SK	1.63	1.13
ClK	0.26	0.10	ClK	4.31	2.71
KK	0.18	0.07	KK	0.99	0.56
CaK	0.32	0.12	CaK	4.40	2.45
TiK	1.04	0.32	FeK	1.51	0.60
FeK	0.37	0.10	ZrL	14.79	3.62
ZrL	4.69	0.75	Totals	100.00	
Totals	100.00				

a.

b.

Figure 11: Elemental Abundance Quantitative Data, Acknowledged on (a): Al-6061 & (b): GCI Coating System

CONCLUSIONS

Few specific conclusions drawn from the present research work are as follows:

- For the current coating system bond coat (Fe38Ni10Al) in case of GCI has contributed more to oxidation also acknowledge weight percent of 1.51 compared to 0.37 in case of Al-6061, in EDS analysis.
- Due to less coating thickness (100µm) the top surfaces are more exposed to bond coat resulting accelerated corrosion in case of GCI compared to two bond coats in case of Al-6061.
- From all the studies it has been concluded that less thicknesses, high porosity with an increase in time lead to oxidation of the bond coat which is visible as brown rust on the top coat. Because of this, 200 µm & 300µm top coat thicknesses of Al₂O₃-ZrO₂.5CaO coatings is more desirable for anti-corrosion related applications.

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